Eur. J. Inorg. Chem. **2013** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2013 · ISSN 1099–0682

SUPPORTING INFORMATION

DOI: 10.1002/ejic.201300309
Title: Hydrogen Evolution Catalyzed by Aluminum-Bridged Cobalt Diglyoximate Complexes
Author(s): Paul Kelley, Michael W. Day, Theodor Agapie*

I. NMR Spectra

II. Electrochemical Data

IV. Crystallographic Information

I. NMR Spectra

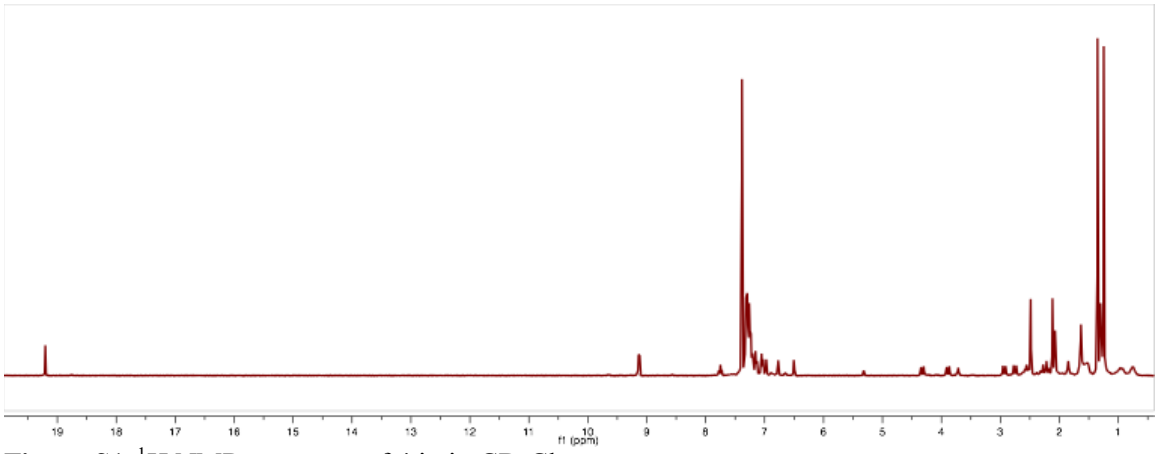

Figure S1. ^{1}H NMR spectrum of **4** in in CD_2Cl_2.

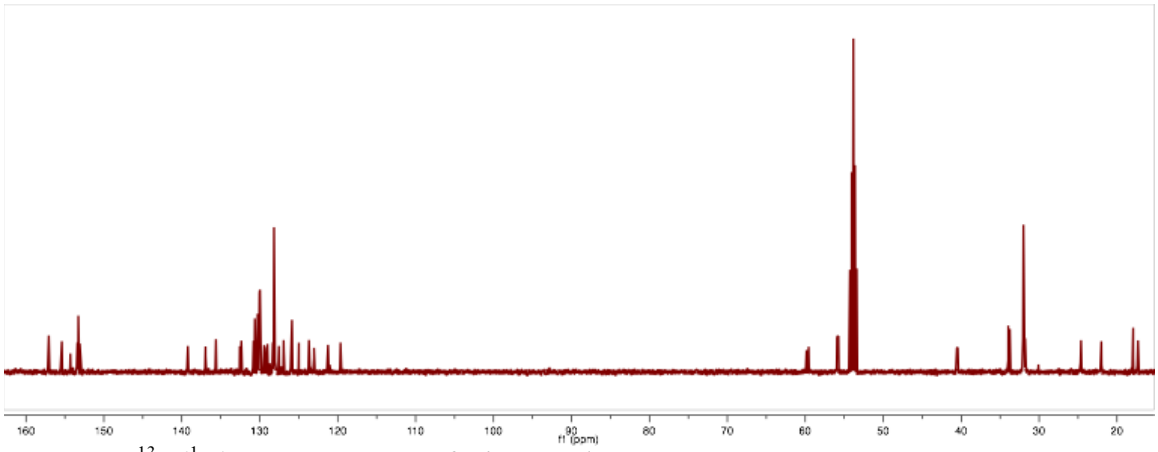

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in CD_2Cl_2.

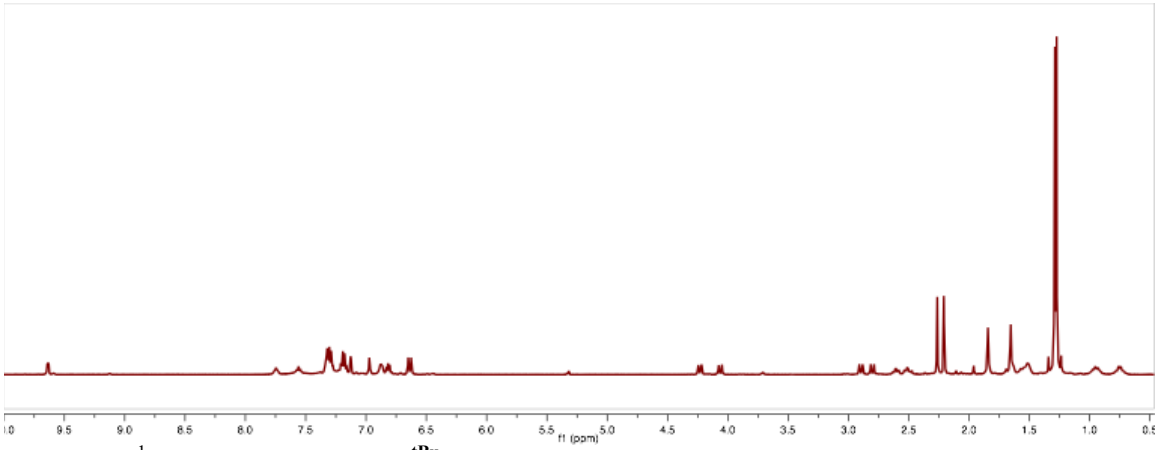

Figure S3. ^{1}H NMR spectrum of $\mathbf{5^{tBu}}$ in CD_2Cl_2.

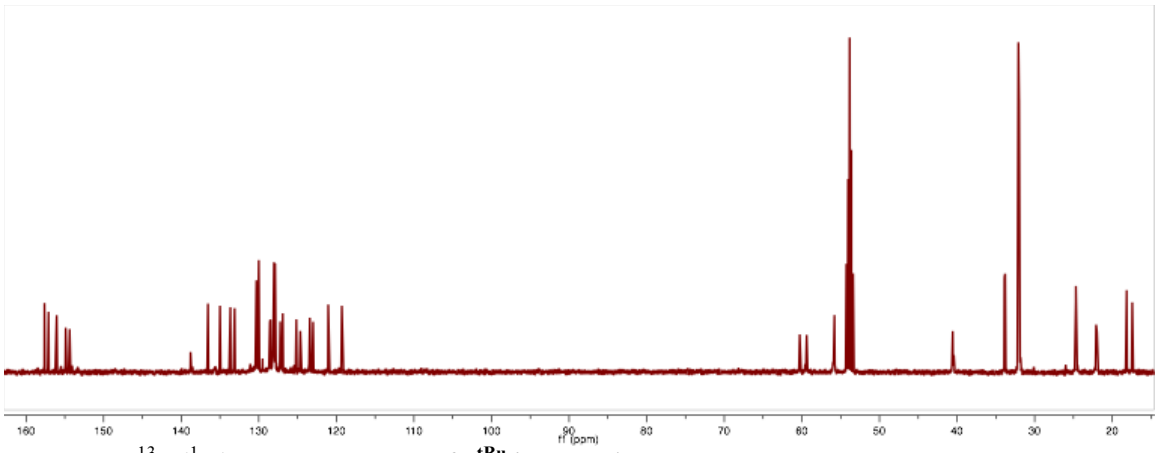

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{5}^{\mathbf{tBu}}$ in CD_2Cl_2.

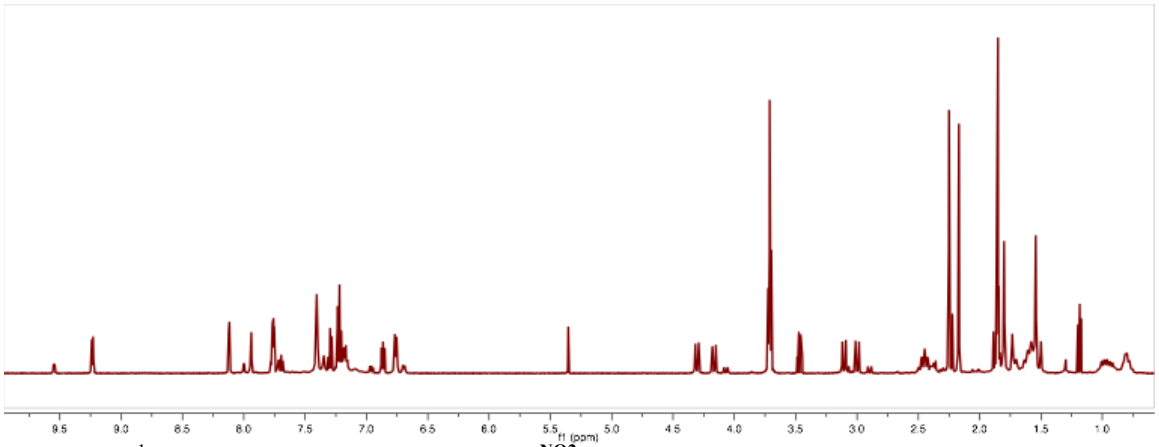

Figure S5. ^{1}H NMR spectrum of crystals of $\mathbf{5}^{\mathbf{NO2}}$ in CD_2Cl_2 (contains THF and Et_2O).

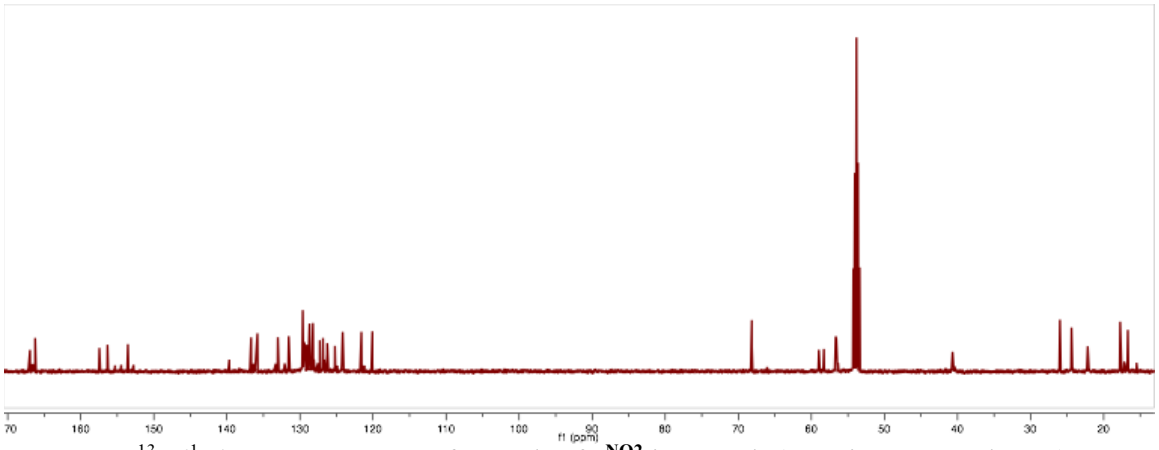

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of crystals of $\mathbf{5}^{\mathbf{NO2}}$ in CD_2Cl_2 (contains THF and Et_2O).

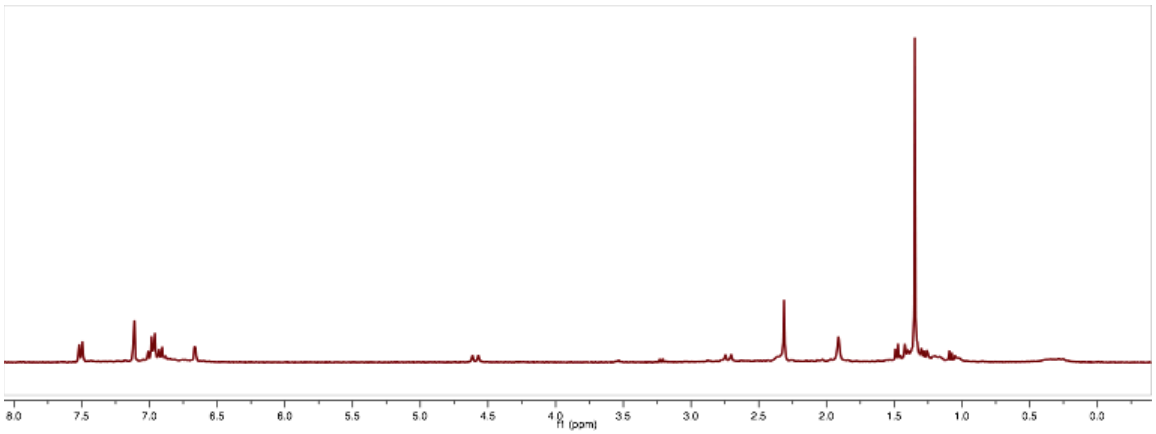

Figure S7. ^{1}H NMR spectrum of **7** in C_6D_6.

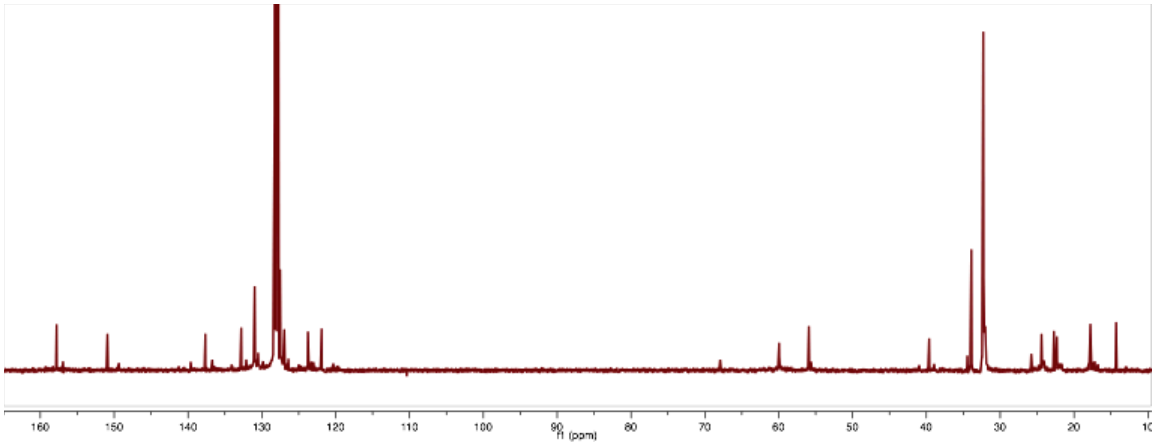

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 (contains pentane and THF).

II. Electrochemical Data

Table S1. Potentials (V) of Synthesized Complexes in DMF (0.1 M NBu_4ClO_4). Reported potentials are referenced to Fc^+/Fc

	E Co^{II}/Co^{I}	*E* H^+_{red}
$\mathbf{3}^{\mathbf{BF2}}$	-0.80	-0.87
$\mathbf{3}^{\mathbf{H}}$	-1.24	-1.29
$\mathbf{5}^{\mathbf{tBu}}$	-1.55	-1.64
4	-1.34	-1.50
$\mathbf{5}^{\mathbf{NO2}}$	-1.35	-1.49

Table S2. Potentials (V) of Synthesized Complexes in MeCN:DCM (0.1 M NBu_4ClO_4). Reported potentials are referenced to Fc^+/Fc

	E H^+_{red}	*E* ArO^-/ArO
$\mathbf{3}^{\mathbf{BF2}}$	-0.76	-
$\mathbf{3}^{\mathbf{H2}}$	-1.26	-
$\mathbf{5}^{\mathbf{tBu}}$	-1.71	0.24/0.47, 0.67
4	-1.52	0.29, 0.64
$\mathbf{5}^{\mathbf{NO2}}$	-1.48	1.03, 1.30
7	-	0.34, 0.66

Table S3. Summary of Bulk Electrolysis Studies[a]

Catalyst	Potential (V vs Fc)	Duration (hr)	Charge Passed (Coulomb)[b]	Faradiac Yield for H_2 (%)	TON
4	-1.62 V	2	38	90%	16
$\mathbf{5}^{\mathbf{tBu}}$	-1.83 V	2	30	70%	12

[a] All bulk electrolysis experiments carried out with 0.1 mM catalyst and 9 mM acid in a MeCN:DCM 1:1 solution of $[nBu_4N][ClO_4]$ (0.1 M) using glassy carbon plate working and counter electrodes with a $Ag/AgNO_3$ (0.01 M) reference electrode. [b] All values corrected for background proton reduction on the glassy carbon plate at the listed potentials. [c] TON calculated from the amount of hydrogen produced during the duration of the bulk electrolysis experiment vs catalyst in solution.

Table S4. Values of i_{cat}/i_p for Synthesized Glyoxime Complexes

Catalyst	i_{cat}/i_p[a] (DMF[b])	i_{cat}/i_p[a] (MeCN/DCM[c])
$\mathbf{3}^{\mathbf{BF2}}$	4	8
$\mathbf{3}^{\mathbf{H}}$	7	17
$\mathbf{5}^{\mathbf{tBu}}$	7	11
4	9	10
$\mathbf{5}^{\mathbf{NO2}}$	5	25[d]

[a] i_{cat} measured at 15 equivalents of acid. [b] trichloroacetic acid was used. [c] p-cyanoanilinium triflate was used. [d] i_{cat} measured at 20 equivalents of acid.

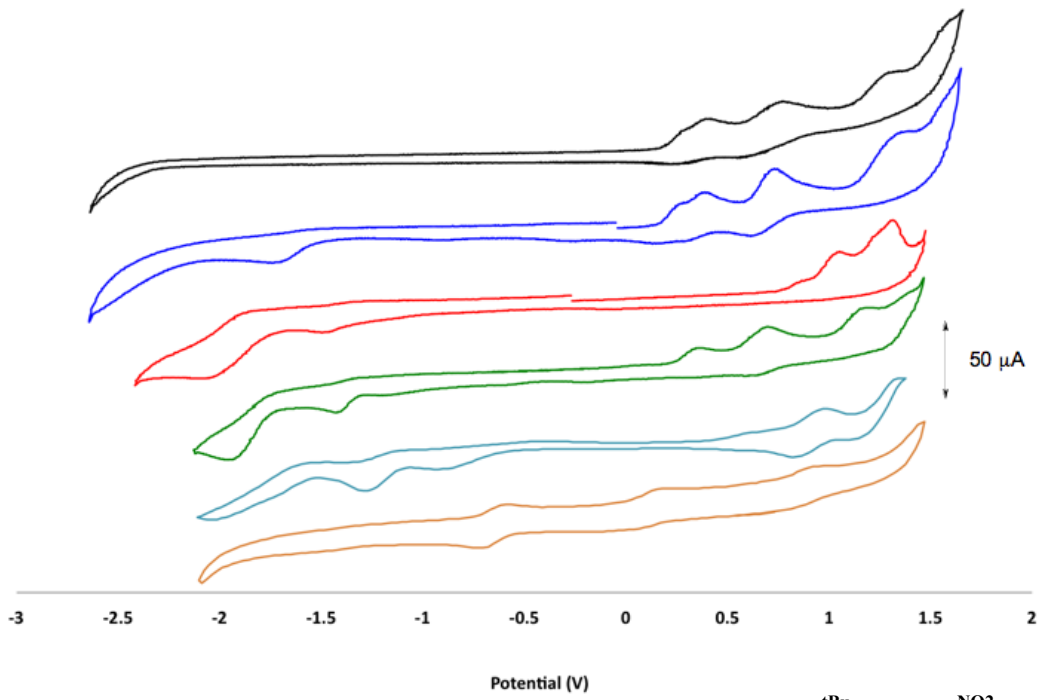

Figure S9. Cyclic voltammograms in 1:1 MeCN:DCM of **7** (black), $\mathbf{5}^{\mathbf{tBu}}$ (blue), $\mathbf{5}^{\mathbf{NO2}}$ (red), **4** (green), $\mathbf{3}^{\mathbf{H2}}$ (turquoise), and $\mathbf{3}^{\mathbf{BF2}}$ (orange) referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

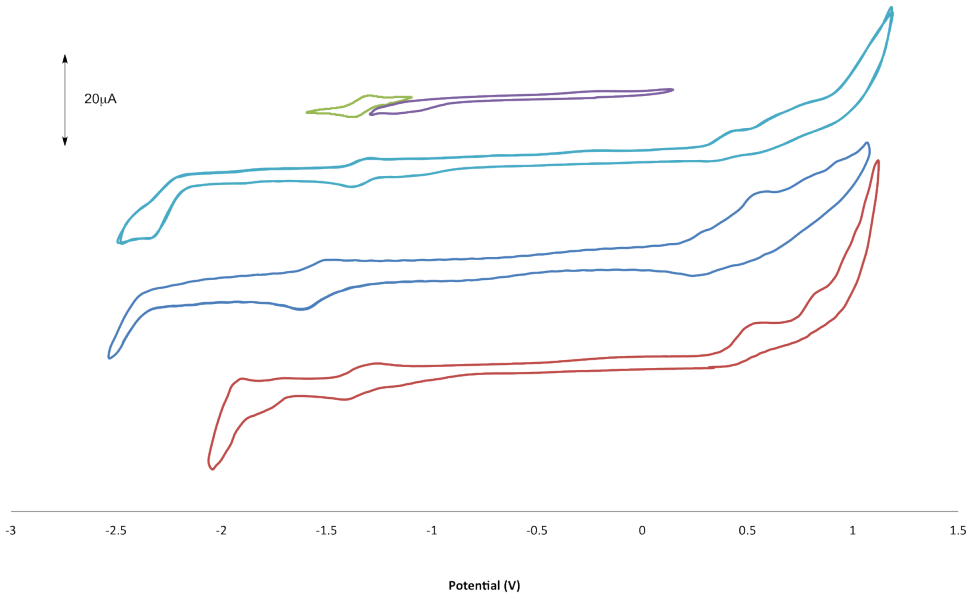

Figure S10. Cyclic voltammograms of $\mathbf{5}^{\mathbf{NO2}}$ (red), $\mathbf{5}^{\mathbf{tBu}}$ (blue), and **4** (turquoise) in DMF. The Co(II/I) (green) and Co(III/II) (purple) waves in **4** are highlighted. All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

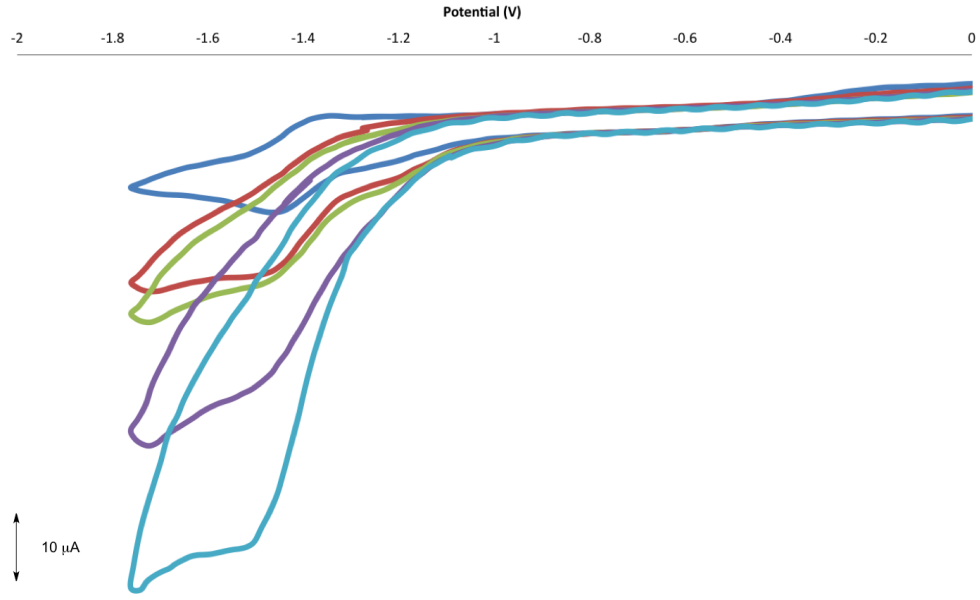

Figure S11. Addition of trichloroacetic acid to **4** at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (green), 11 mM acid (purple), 15 mM acid (turquoise). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

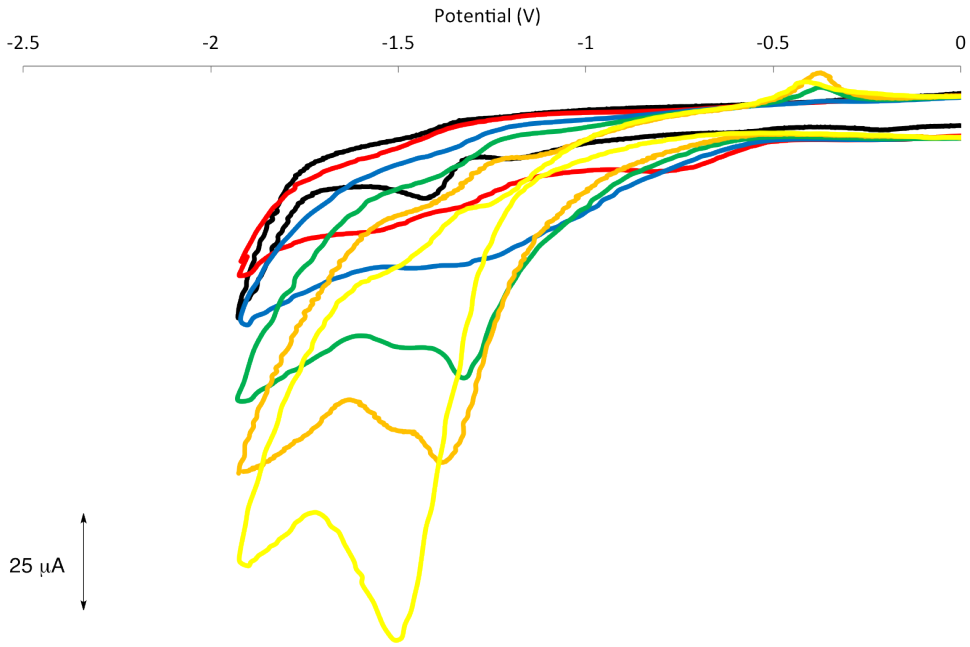

Figure S12. Addition of p-cyanoanilinium triflate to **4** at (1 mM) in 1:1 MeCN:DCM, No acid (black), 3 mM acid (red), 7 mM acid (blue), 11 mM acid (green), 15 mM acid (orange), 20 mM acid (yellow). All waves referenced to Fc^+/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

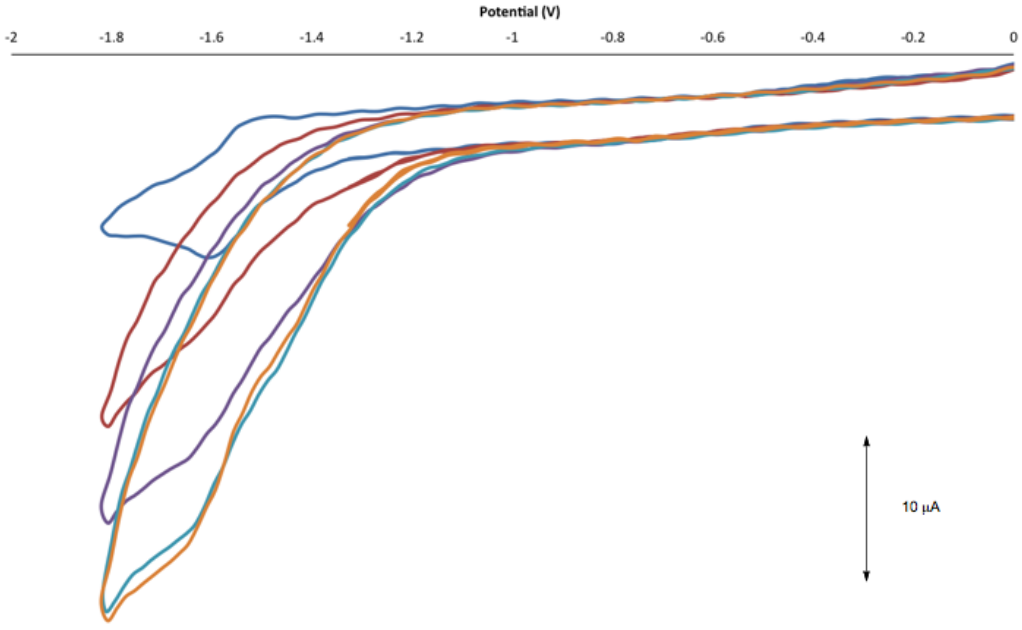

Figure S13. Addition of trichloroacetic acid to $\mathbf{5}^{\mathbf{tBu}}$ at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (purple), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^+/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

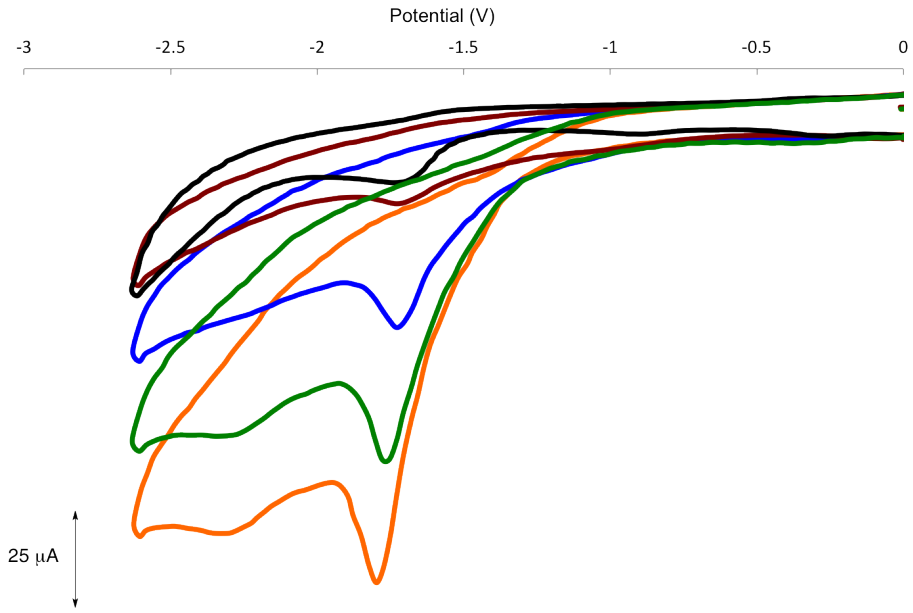

Figure S14. Addition of p-cyanoanilinium triflate to $\mathbf{5}^{\mathbf{tBu}}$ at (1 mM) in 1:1 MeCN:DCM, No acid (black), 3 mM acid (red), 7 mM acid (blue), 11 mM acid (green), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

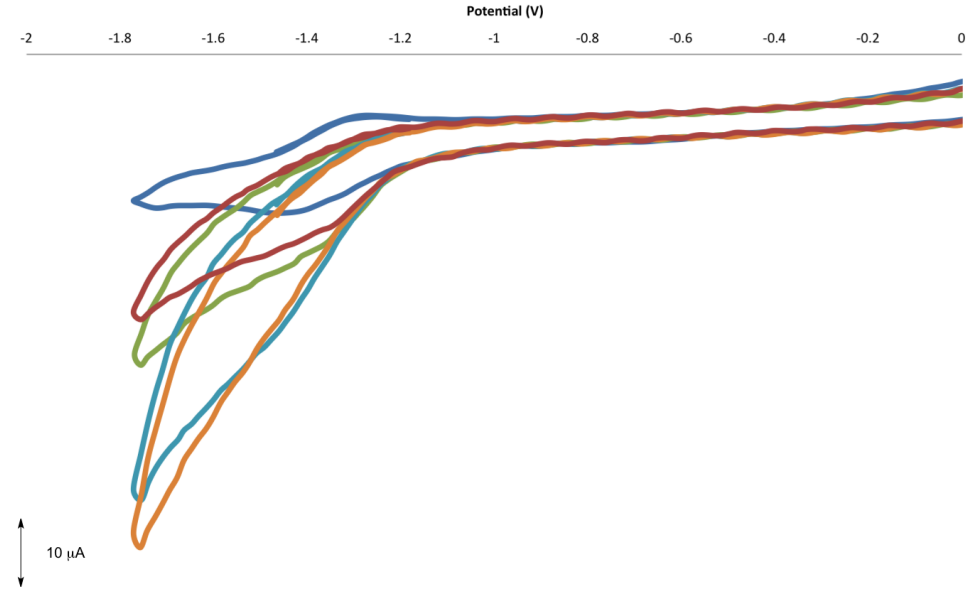

Figure S15. Addition of trichloroacetic acid to $\mathbf{5}^{\mathbf{NO2}}$ at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (green), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

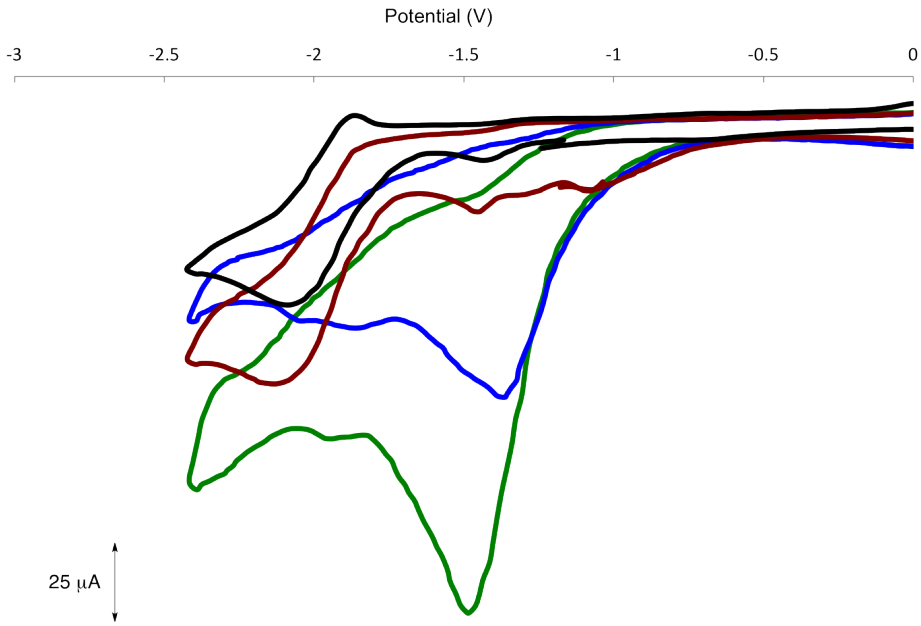

Figure S16. Addition of p-cyanoanilinium triflate to $\mathbf{5}^{\mathbf{NO2}}$ at (1 mM) in MeCN:DCM, No acid (black), 2 mM acid (red), 10 mM acid (blue), 20 mM acid (green). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

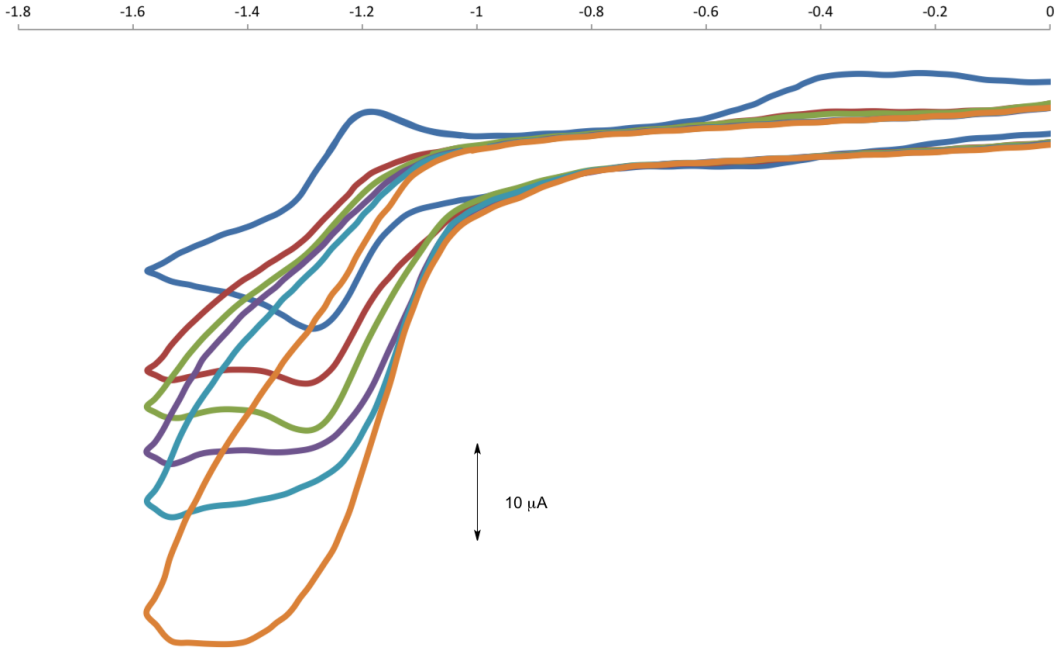

Figure S17. Addition of trichloroacetic acid to $\mathbf{3}^{\mathbf{H}}$ at (1 mM) in DMF, No acid (blue), 1.5 mM acid (red), 3 mM acid (green), 6 mM acid (purple), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

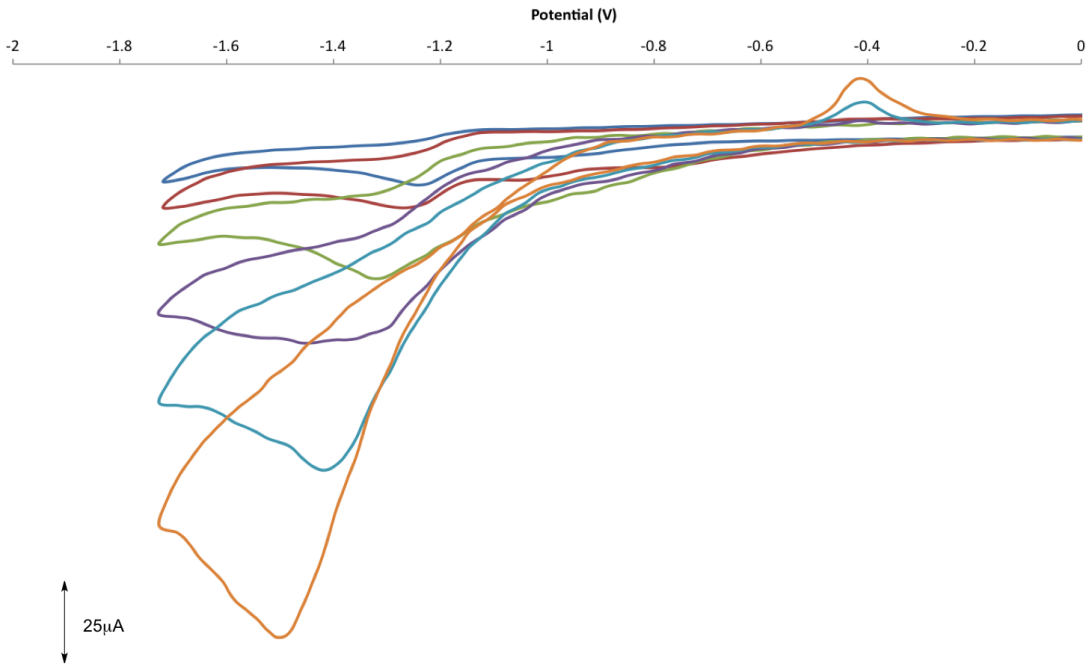

Figure S18. Addition of p-cyanoanilinium triflate to $\mathbf{3}^{\mathbf{H}}$ at (1 mM) in MeCN:DCM, No acid (blue), 1.5 mM acid (red), 3 mM acid (green), 6 mM acid (purple), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

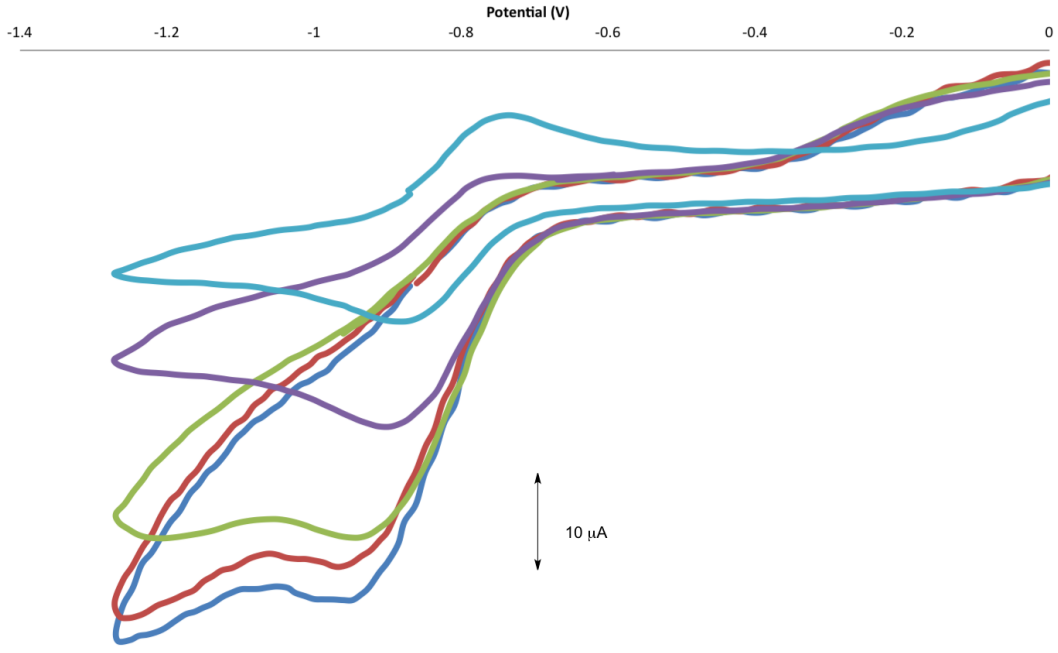

Figure S19. Addition of trichloroacetic acid to $\mathbf{3}^{\mathbf{BF2}}$ at (1 mM) in DMF, No acid (turquoise), 3 mM acid (purple), 6 mM acid (green), 10 mM acid (red), 15 mM acid (blue). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in DMF.

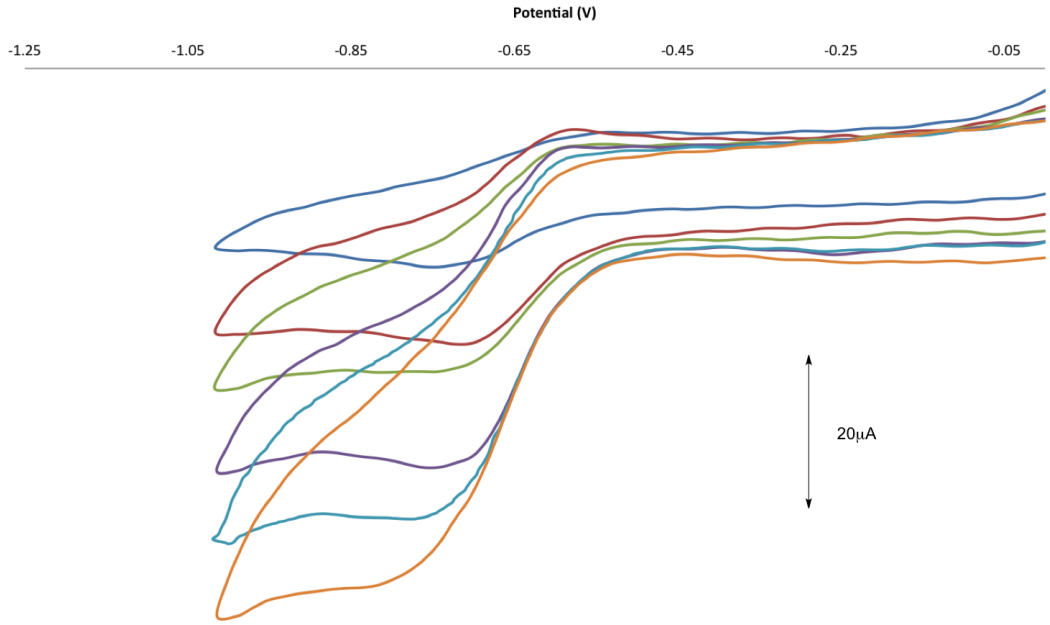

Figure S20. Addition of p-cyanoanilinium triflate to $\mathbf{3}^{\mathbf{BF2}}$ at (1 mM) in MeCN:DCM, No acid (blue), 1.5 mM acid (red), 3 mM acid (green), 6 mM acid (purple), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc^{+}/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu_4ClO_4 in MeCN:DCM.

IV. Crystallographic Data

Table S4. *Crystal and refinement data for* ***4****,* ***5^{tBu}****, and* ***5^{NO2}***

	4	**5^{tBu}**	**5^{NO2}**
CCDC Deposition #	861068	863680	862110
Empirical formula	$C_{65}H_{74}ClN_7O_6AlCo \bullet C_5H_{12}$	$C_{97}H_{121}N_9O_8Al_2ClCo \bullet 1.55(C_5H_{12}) \bullet 0.45(C_6H_6)$	$C_{81}H_{84}N_{13}O_{16}Al_2ClCo$
Formula weight	1242.82	1836.69	1643.95
Crystallization Solvent	Benzene/pentane	Benzene/pentane	THF/pentane (solvent flattened)
Crystal Habit	Block	Plate	Block
Crystal size, mm^3	0.34 x 0.27 x 0.21	0.33 x 0.32 x 0.11	0.41 x 0.29 x 0.24
Crystal color	Yellow/brown	Brown	Dark brown
q range for lattice determination	2.31 to 27.65°	2.31 to 27.65°	2.17 to 28.85°
a, Å	18.2062(9)	33.3885(19)	11.8585(5)
b, Å	18.3182(9)	12.4645(7)	19.9092(8)
c, Å	20.2299(10)	26.8733(15)	22.2150(9)
a, °	90	90	90
b, °	90	111.652(3)	92.687(2)
g, °	90	90	90
Volume, $Å^3$	6746.8(6)	10394.8(10)	5239.0(4)
Z	4	4	2
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\ 2_12_12_1$	C 2	$P\ 2_1$
Density (calculated)	1.224 Mg/m^3	1.174 Mg/m^3	1.042 Mg/m^3
F(000)	2640	3936	1718
q range for data collection, °	1.87 to 30.56	1.63 to 28.47	1.84 to 27.54
Completeness to q = 26.43°	99.9%	99.1%	99.7%
Index ranges	$-26 \le h \le 26$ $-26 \le k \le 25$ $-28 \le l \le 28$	$-44 \le h \le 44$ $-16 \le k \le 16$ $-35 \le l \le 35$	$-15 \le h \le 15$ $-25 \le k \le 25$ $-28 \le l \le 28$
Data collection scan type	w scans; 11 settings	w scans; 19 settings	w scans; 10 settings
Reflections collected	180165	194954	109398
Independent reflections	20651 [R_{int}= 0.0506]	25991 [R_{int}= 0.0811]	24099 [R_{int}= 0.0695]
Absorption coefficient, mm^{-1}	0.362	0.266	0.264
Absorption correction	None	None	None
Max. and min. transmission	0.9278 and 0.8868	0.9714 and 0.9174	0.9394 and 0.8996
Hydrogen placement	Geometric positions	Geometric positions	Geometric positions
Structure refinement	SHELXL-97	SHELXL-97	SHELXL-97

program	(Sheldrick, 2008)	(Sheldrick, 2008)	(Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data / restraints / parameters	20651 / 0 / 804	25991 / 117 / 1212	24099 / 1 / 1035
Treatment of hydrogen atoms	Riding	Riding	Riding
Goodness-of-fit on F2	3.590	3.008	2.457
Final R indices [I>2s(I), 4802 reflections]	R1 = 0.0610 *w*R2 = 0.0704	R1 = 0.0671 *w*R2 = 0.1146	R1 = 0.0637 *w*R2 = 0.1021
R indices (all data)	R1 = 0.0858 *w*R2 = 0.0711	R1 = 0.0787 *w*R2 = 0.1146	R1 = 0.0778 *w*R2 = 0.1033
Type of weighting scheme used	Sigma	Sigma	Sigma
Weighting scheme used	$w=1/s^2(Fo^2)$	$w=1/s^2(Fo^2)$	$w=1/s^2(Fo^2)$
Max shift/error	0.000	0.004	0.000
Average shift/error	0	0	0
Largest diff. peak and hole, e.Å^{-3}	1.668 and -0.697	1.569 and -0.962	1.241 and -0.920
Type of diffractometer	Bruker KAPPA APEX II	Bruker KAPPA APEX II	Bruker KAPPA APEX II
Wavelength, Å MoKa	0.71073	0.71073	0.71073
Data Collection Temperature	100(2) K	100(2) K	100(2) K
Structure solution program	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods	Direct methods	Direct methods
Secondary solution method	Difference Fourier map	Difference Fourier map	Difference Fourier map

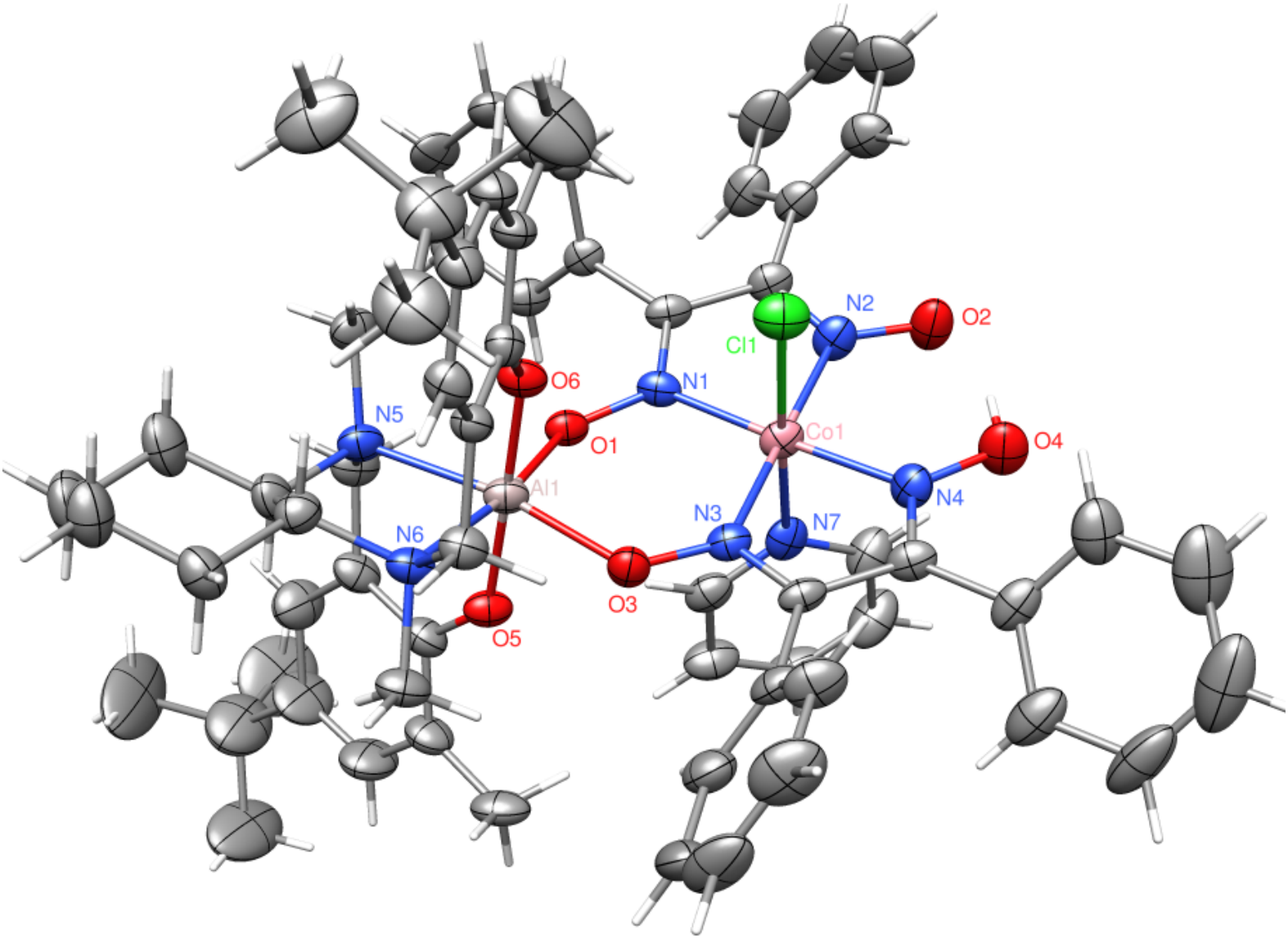

Figure S21. Structural drawing of **4** with 50% thermal probability ellipsoids.

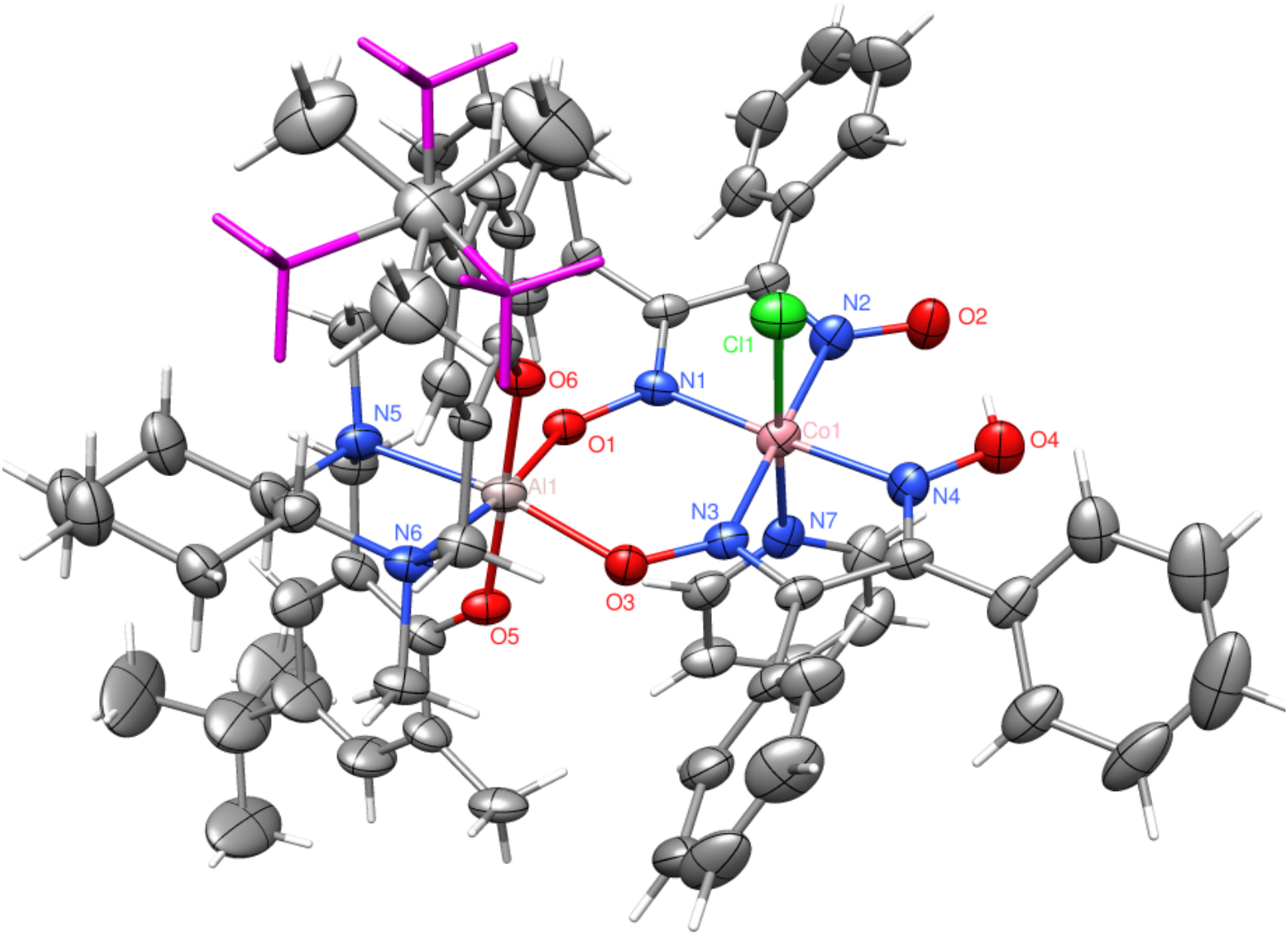

Figure S22. Structural drawing of **4** with 50% thermal probability ellipsoids showing disorder in the *tert*-butyl group.

Special Refinement Details for 4. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. One t-Bu group is disordered, C42-44, and was refined anisotropically without restraint while constraining the total population of the group to one.

Table S5. Selected bond lengths **[Å]** and angles **[°]** for **4.**

Co(1)-N(1)	1.892(2)	N(1)-Co(1)-N(4)	177.70(10)
Co(1)-N(4)	1.899(2)	N(1)-Co(1)-N(2)	81.41(9)
Co(1)-N(2)	1.905(2)	N(4)-Co(1)-N(2)	97.18(9)
Co(1)-N(3)	1.926(2)	N(1)-Co(1)-N(3)	100.45(9)
Co(1)-N(7)	1.958(2)	N(4)-Co(1)-N(3)	80.82(9)
Co(1)-Cl(1)	2.2186(7)	N(2)-Co(1)-N(3)	175.73(9)
Al(1)-O(6)	1.7984(17)	N(1)-Co(1)-N(7)	90.59(8)
Al(1)-O(5)	1.8247(18)	N(4)-Co(1)-N(7)	91.31(8)
Al(1)-O(1)	1.8656(17)	N(2)-Co(1)-N(7)	92.88(9)
Al(1)-O(3)	1.8918(17)	N(3)-Co(1)-N(7)	90.94(8)
Al(1)-N(5)	2.127(2)	N(1)-Co(1)-Cl(1)	91.05(6)
Al(1)-N(6)	2.130(2)	N(4)-Co(1)-Cl(1)	87.03(6)
		N(2)-Co(1)-Cl(1)	86.34(7)
		N(3)-Co(1)-Cl(1)	89.78(6)
		N(7)-Co(1)-Cl(1)	178.06(7)
		O(6)-Al(1)-O(5)	178.77(9)
		O(6)-Al(1)-O(1)	89.91(8)
		O(5)-Al(1)-O(1)	91.10(7)
		O(6)-Al(1)-O(3)	95.66(8)
		O(5)-Al(1)-O(3)	84.89(8)
		O(1)-Al(1)-O(3)	97.97(8)
		O(6)-Al(1)-N(5)	91.48(8)
		O(5)-Al(1)-N(5)	87.85(8)
		O(1)-Al(1)-N(5)	88.64(8)
		O(3)-Al(1)-N(5)	170.25(9)
		O(6)-Al(1)-N(6)	87.96(8)
		O(5)-Al(1)-N(6)	90.95(8)
		O(1)-Al(1)-N(6)	171.87(9)
		O(3)-Al(1)-N(6)	90.05(8)
		N(5)-Al(1)-N(6)	83.57(8)

Symmetry transformations used to generate equivalent atoms:

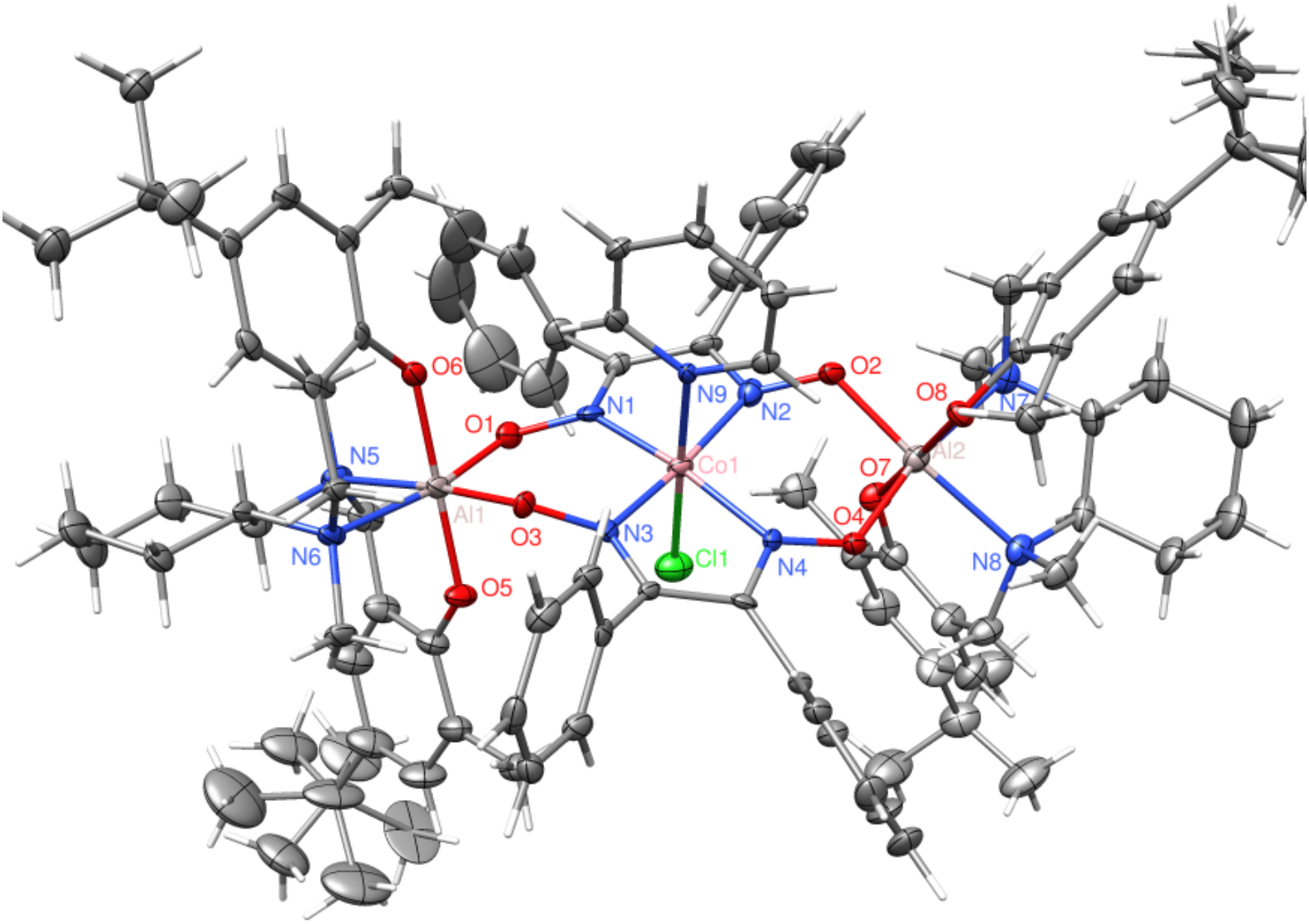

Figure S23. Structural drawing of $\mathbf{5^{tBu}}$ with 50% thermal probability ellipsoids.

Special Refinement Details for $\mathbf{5^{tBu}}$. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. This sample is multiple crystals but we were not able to integrate each component separately. The solvent region is disordered, one site contains pentane and the other site contains a mixture of benzene and pentane. The geometry of the pentanes were restrained and the benzene was constrained to an ideal hexagon. The mixed solvent site was refined with isotropic temperature factors. Additional disorder is observed in two tertiary butyl groups. Anisotropic displacement parameters of these two groups were restrained to approximate isotropic behavior.

Table S6. Selected bond lengths **[Å]** and angles **[°]** for $\mathbf{5}^{\mathbf{tBu}}$.

Co(1)-N(3)	1.893(3)	N(3)-Co(1)-N(2)	171.00(11)
Co(1)-N(2)	1.906(3)	N(3)-Co(1)-N(1)	97.77(12)
Co(1)-N(1)	1.919(3)	N(2)-Co(1)-N(1)	82.47(12)
Co(1)-N(4)	1.931(3)	N(3)-Co(1)-N(4)	82.26(12)
Co(1)-N(9)	1.976(3)	N(2)-Co(1)-N(4)	99.12(12)
Co(1)-Cl(1)	2.2172(10)	N(1)-Co(1)-N(4)	169.67(11)
		N(3)-Co(1)-N(9)	85.42(11)
		N(2)-Co(1)-N(9)	85.60(11)
		N(1)-Co(1)-N(9)	95.95(11)
		N(4)-Co(1)-N(9)	94.35(11)
		N(3)-Co(1)-Cl(1)	94.34(8)
		N(2)-Co(1)-Cl(1)	94.65(9)
		N(1)-Co(1)-Cl(1)	84.91(8)
		N(4)-Co(1)-Cl(1)	84.78(8)
		N(9)-Co(1)-Cl(1)	179.13(9)

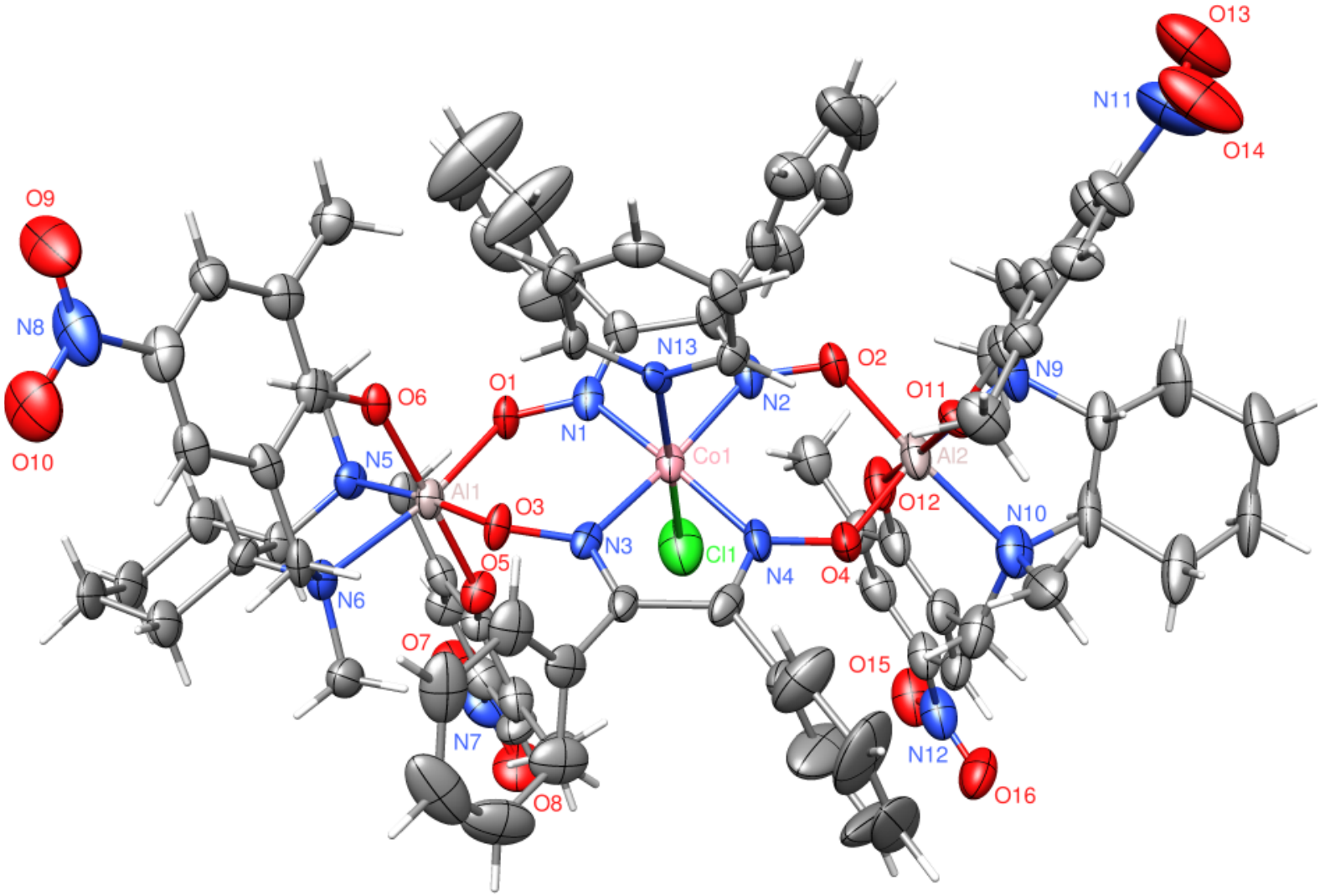

Figure S24. Structural drawing of $\mathbf{5}^{NO2}$ with 50% thermal probability ellipsoids.

Special Refinement Details for $\mathbf{5}^{NO2}$. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The solvent region is very disordered and we were unable to obtain a satisfactory model. Therefore the observed intensities were adjusted to return zero density in the calculated electron density map using SQUEEZE. The volume of the solvent region is 1823.8Å^3 (34.8% of total cell volume) and a total of 399 electrons were attributed to this area. This is consistent with the electron count expected for 10 solvents sites containing THF/pentane.

.

Table S7. Selected bond lengths **[Å]** and angles **[°]** for $\mathbf{5^{NO2}}$.

Co(1)-N(4)	1.898(3)	N(4)-Co(1)-N(3)	82.69(12)
Co(1)-N(3)	1.908(3)	N(4)-Co(1)-N(1)	172.18(11)
Co(1)-N(1)	1.909(3)	N(3)-Co(1)-N(1)	98.55(12)
Co(1)-N(2)	1.927(3)	N(4)-Co(1)-N(2)	98.67(12)
Co(1)-N(13)	2.033(2)	N(3)-Co(1)-N(2)	171.68(11)
Co(1)-Cl(1)	2.2121(10)	N(1)-Co(1)-N(2)	81.23(12)
		N(4)-Co(1)-N(13)	95.15(10)
		N(3)-Co(1)-N(13)	85.46(10)
		N(1)-Co(1)-N(13)	92.64(10)
		N(2)-Co(1)-N(13)	86.24(11)
		N(4)-Co(1)-Cl(1)	86.46(9)
		N(3)-Co(1)-Cl(1)	94.83(8)
		N(1)-Co(1)-Cl(1)	85.74(8)
		N(2)-Co(1)-Cl(1)	93.45(8)
		N(13)-Co(1)-Cl(1)	178.38(8)